Resonance Fluorescence and Absorption Spectra of Molecular Iodine: Identification and Molecular Assignment

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Summary Molecular levels in the $B^3\Pi_{0^+u}$ state excited by several Ar$^+$ and Kr$^+$ laser lines and the Cd I emission line at 5086 Å have been positively identified following an extended rotational analysis of bands of the B–X system of I_2.

RECENTLY there have been several investigations of laser-excited resonance fluorescence [1–8] of the visible system of iodine $B^3\Pi_{0^+u}$ — $X^1\Sigma_g^+$ and of energy-transfer processes[9,10] involving monochromatically excited rotational vibrational levels of the $B^3\Pi_{0^+u}$ state. However some of the published spectroscopic assignments of the resonance fluorescence series are incorrect, particularly those for the high v' levels. In the course of rotational analysis with the aim of constructing an accurate experimental R.K.R. potential energy curve for the $B^3\Pi_{0^+u}$ state we have been able to identify unambiguously all the molecular levels excited by the various Ar$^+$ and Kr$^+$ laser lines and the Cd I emission line at 5086 Å.

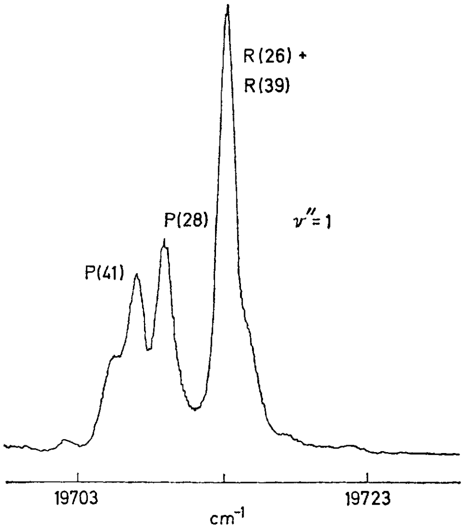

FIGURE. *Structure of the resonance fluorescence series of* I_2 *for* v'' = 1 *excited by the* 5017 Å Ar$^+$ *laser line. Excitation is in* R(39) *of the* 64–0 *band and* R(26) *of the* 62–0 *band of* $B^3\Pi_{0^+u}$ $-X^1\Sigma^+_g$.

The absorption spectrum of iodine was photographed on Ilford N50 and R52 plates in a Jarrell–Ash 3·4 m. Mark II Ebert spectrograph with a reciprocal dispersion of about 0·48 Å/mm in the region 6000—4980 Å. Fe hollow-cathode lines were used as standards. Various absorption path-lengths were used in the different regions of the spectrum in order to reduce the degree of overlapping of lines. For the bands near the dissociation limit the iodine cell was cooled to temperatures somewhat below room temperature.

Summary of resonance fluorescence series and molecular assignment of the $B^3\Pi_{0^+u}$ — $X^1\Sigma^+_g$ *system of iodine*

Exciting line	Molecular excitation[a] v', v''	Measured frequency cm^{-1}	Ref.
Ar$^+$ Laser 5017 Å 19926·04 cm^{-1}	R(39) 64–0 R(26) 62–0	19925·97 19925·97	4, 6
Cd I 5086 Å 19657·02 cm^{-1}	R(40) 50–0 P(9) 49–0	19656·90 19656·98	7, 9
Ar$^+$ Laser 5145 Å 19429·73 cm^{-1}	$\left.\begin{array}{l}\text{R(15)}\\ \text{P(13)}\end{array}\right\}$ 43–0	19429·81	1, 4—7
Hg I 5461 Å 18307·48 cm^{-1}	R(33) 25–0		11
Kr$^+$ Laser 5682 Å 17594·93 cm^{-1}	P(96) 18–0 P(37) 17–0	17594·93 17594·93	2
Ne Laser 6328 Å 15798·02 cm^{-1}	R(127) 11–5 P(33) 6–3		3, 5, 7, 8

[a] The J numbering of the R and P lines is for the ground state.

Rotational analysis of many bands with $16 \leqslant v' \leqslant 66$ has now been completed.

The resonance fluorescence spectra excited by the 5017 and 5145 Å Ar^+ laser lines were recorded with a Spex 1401 spectrometer. These fluorescence series proved to be an important aid in the rotational analysis of the bands at high v' levels.

A portion of the resonance fluorescence spectrum from the 5017 Å Ar^+ line which excites both the R(39) line of the 64–0 band and the R(26) line of the 62–0 band is shown in the Figure. Halldorsson and Menke[6] have reported a tentative and incomplete assignment of only the stronger fluorescence series. However, the presence of two series is in complete agreement with the present analysis.

A summary of the resonance fluorescence series and molecular assignment of the $B^3\Pi_{0^+u} - X^1\Sigma_g{}^+$ system of iodine is given in the Table. Assignments for the mercury green line at 5461 Å and the Ne laser line at 6328 Å are also included for the sake of completeness.

Sakurai and Broida[2] have reported two strong fluorescence series excited by the 5682 Å Kr^+ laser line (17594·93 cm^{-1}). Their identification of the excited molecular levels for these two series as $v' = 16$, $J' = 38 \pm 1$ and $v' = 17$, $J' = 100 \pm 3$ both arising from $v'' = 0$ appears to be erroneous (Table). The fact that these two series are very strong is consistent with the measured frequency of 17594·93 cm^{-1} for the blend of P(96) of the 18–0 band and P(37) of the 17–0 band.

The identification of the molecular lines excited by the 5145 Å Ar^+ laser line as R(15) and P(13) of the 43–0 band is in agreement with that of Halldorsson and Menke[6] whose assignment was based on interferometric measurements of the R–P doublet separations in the fluorescence series. On the other hand, our identification of the molecular lines and rotational analysis of the 43–0 band do not agree with those reported by Steinfeld, Campbell, and Weiss.[7]

Excitation of iodine by the 5086 Å Cd I line has been attributed by Pringsheim[12] to $v' = 50$, $J' = 8$ and $v' = 51$, $J' = 43$ of the $B^3\Pi_{0^+u}$ state. Recently this has been reassigned[7,9] to $v' = 50$, $J' = 29$ and $v' = 53$, $J' = 65$ on the basis of long extrapolations of experimental data. This reassignment appears to be incorrect and, taking into account the revised vibrational numbering in $B^3\Pi_{0^+u}$, it appears that Pringsheim's original assignment was not far wrong.

Some of the conclusions of previous work on energy transfer processes using monochromatic radiation may need revision in the light of the new assignments.

We thank Professor I. R. Beattie and Dr. Gilson for their help in recording the fluorescence spectra. We also thank the Science Research Council for a grant and Dr. R. F. Barrow for his interest.

(*Received*, 29*th June* 1972; *Com.* 1134.)

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